

Temperature and Pressure Dependence of Self Diffusion in Octamethylcyclotetrasiloxane and Hexamethylcyclotrisilazane

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The pressure dependence of the self diffusion coefficient D for octamethylcyclotetrasiloxane and hexamethylcyclotrisilazane has been determined by the NMR spin echo technique with pulsed magnetic field gradients at pressures up to 200 MPa and at temperatures between 490 K and 290 K.

The data extend partially into the deeply supercooled range. The isobaric temperature dependence of these data is quantitatively described by the empirical Vogel-Fulcher-Tammann equation. For both substances the melting pressure curves were determined in addition.

Introduction

The quantitative description of the T, p dependence of the self diffusion coefficient D of neat liquids provides a good test for the validity of the various theories and models for the dynamics of liquids [1, 2].

In the last years our group has studied the T, p dependence of D for a variety of halomethane derivatives [3, 4]. It was found that these liquids are well represented by modifications of hard sphere descriptions [5, 6], and it proved necessary to include attractive interactions for a quantitative representation of the data [6]. These studies were recently extended to some hydrogen bonded liquids like small monohydric alcohols [7] and supercooled water [8, 9] in order to test the limits of applicability of hard sphere models and to learn about the possible extensions for this description. The two compounds studied here represent large, heavy unpolar molecules of approximately spherical shape and provide an additional test for the transport models cited above.

Materials and Methods

Octamethylcyclotetrasiloxane (OMCTS) purum and hexamethylcyclotrisilazane (HMS) purum were purchased from Fluka AG (Buchs, Switzerland). The substances were stored over molecular sieve 3 Å and used without further purification. The compounds

were studied in strengthened glass capillaries with i.d. between 100 and 200 µm and o.d. of 1.5 mm.

Details of the apparatus [9] and the filling procedure [10] have been published. The self diffusion coefficients were obtained in a Bruker MSL-300 spectrometer operating at a proton frequency of 300.1 MHz in a home built probe head in a Hahn spin echo pulse sequence by the pulsed field gradient method as introduced by Stejskal and Tanner [11]. In the presence of the field pulses, the decay of the echo amplitude A is given by

$$A(2\tau) = A(0) \exp(-2\tau/T_2) \exp(-\gamma^2 \delta^2 g^2 D(\Delta - \delta/3)), \quad (1)$$

where τ is the time between the 90° and 180° pulse, D the self diffusion coefficient, δ the duration of the gradient pulse, Δ the time between the two gradient pulses and g the gradient strength, given by $g = kI$. Here I is the current intensity and k the coil constant, which has been obtained from a calibration with the known diffusion coefficient of water at ambient pressure and 298 K [12] and controlled by benzene data, known from tracer measurements [13].

D was determined by recording 10–15 spin-echos with increasing g values while holding all other variables constant. The following Fourier transformation of the echos facilitates the analysis of the data and permits the detection of impurities. The measured diffusion coefficients are regarded as reliable to $\pm 5\%$.

In the strengthened glass cell construction used, only the lower part of the glass capillary is thermostated by a flow of cooled or heated nitrogen, and one has to avoid crystallization of the sample under study by heating the upper part of the capillary and the autoclave above the melting pressure curve. Since

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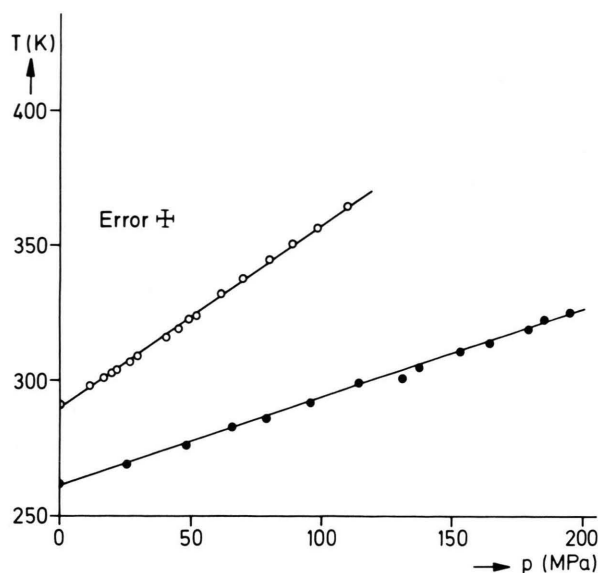


Fig. 1. Melting point vs. pressure of hexamethylcyclotrisilazane (full circles) and octamethylcyclotetrasiloxane (open circles).

Table 1. Fitparameter T_0 , D_0 , and B of the VTF equation.

p [MPa]	0.1	25	50	100	150	200
<i>Substance: HMS</i>						
T_0 [K]	102	—	133	159	162	159
D_0 [10^{-9} m ² /s]	44.2	—	17.2	9.2	8.06	8.68
B [K]	858	—	669	554	601	703
<i>Substance: OMCTS</i>						
T_0 [K]	52	81	103	165	199	237
D_0 [10^{-9} m ² /s]	81.3	31.3	16.6	4.63	2.42	1.32
B [K]	1311	1049	893	537	417	291

only the ambient pressure melting temperature for OMCTS and HMS were known, we studied the pressure dependence of the melting point by cooling the lower end of the high pressure glass capillary in a carbondioxide/ethanol mixture until the sample crystallized and observing visually the melting process during slow heating. Both substances tend to supercooling, and thus only the melting process could be followed with accuracy. In Fig. 1 the data obtained are collected.

Results and Discussion

The Figs. 2 and 3 collect the self diffusion coefficient vs. pressure isotherms for HMS and OMCTS. In Fig. 5 previously published data for OMCTS are included for comparison [14–16]. The data from the different sources agree within the limits of the experimental errors stated by the authors.

Both substances can be readily supercooled. In the case of HMS the 50 MPa isobar of D could be followed to 70 K below the melting temperature. The slope of the isobars increases with falling temperature, this is most obvious for the HMS-data which extend over the largest temperature range.

Figures 4 and 5 give the isobaric Arrhenius plots of the self diffusion coefficient. They all show a definite curvature, the slope increasing with falling temperature and increasing pressure. This type of behaviour is typical for undercooled viscous liquids and is usually well represented by the empirical VTF equation [17–19]

$$D = D_0 \exp(-B/T - T_0), \quad (2)$$

where T_0 is interpreted as the ideal glass transition temperature, where all translational molecular mobility

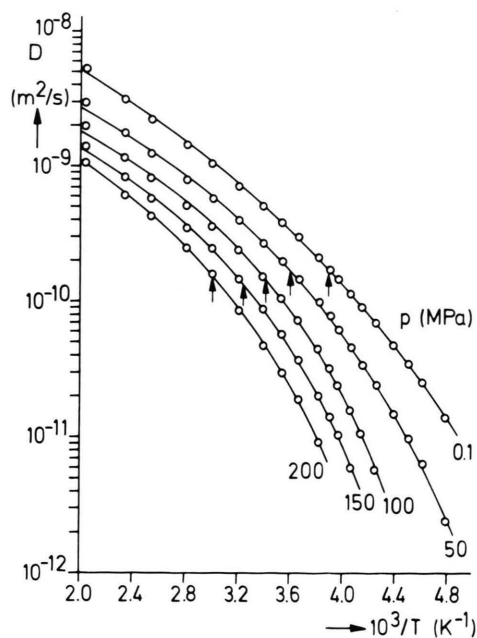


Fig. 4. Arrhenius plot of self diffusion coefficient isobars for hexamethylcyclotrisilazane. The lines drawn through the experimental points result from a least squares fit to the VTF equation. The arrows indicate the melting temperatures at the various pressures.

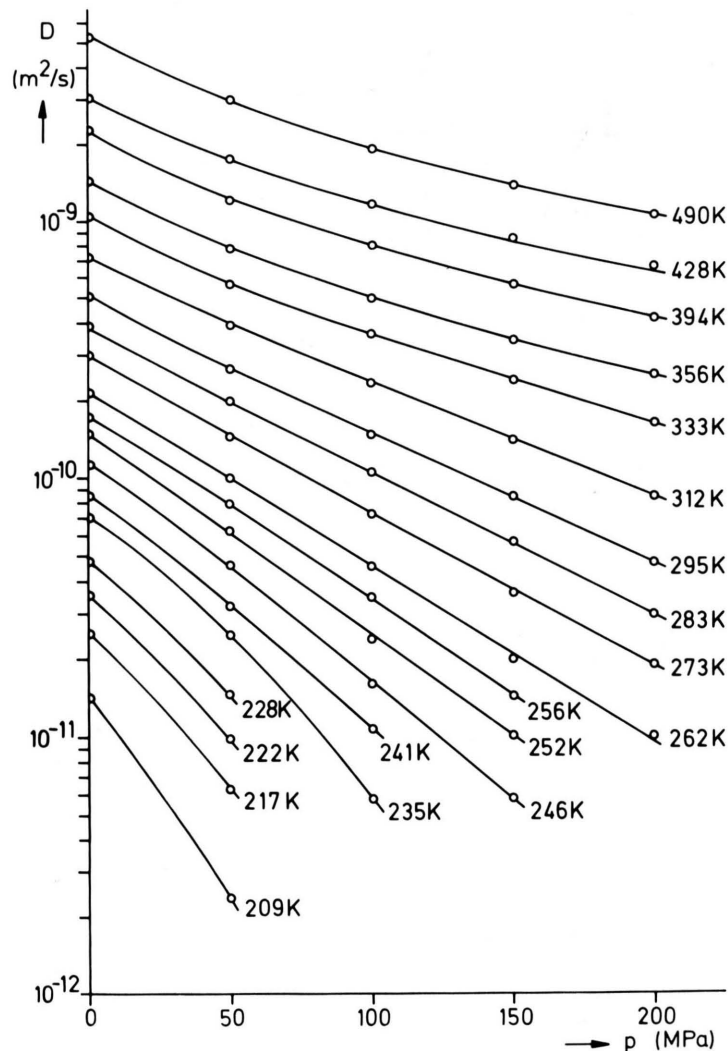


Fig. 2. Self diffusion coefficient vs. pressure isotherms of hexamethylcyclotrisilazane.

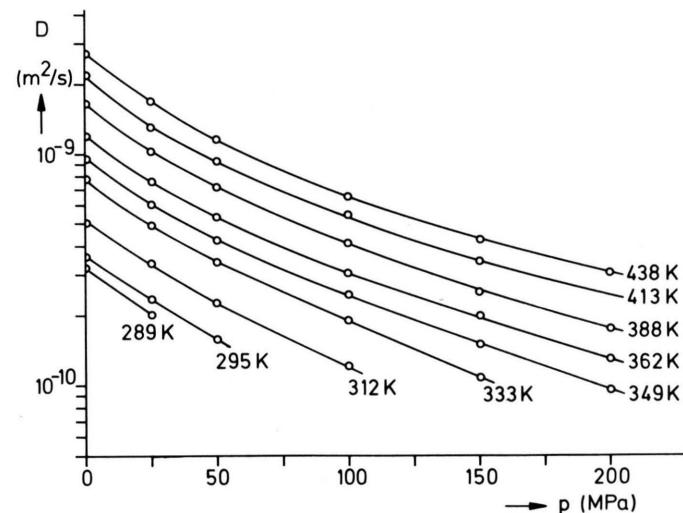


Fig. 3. Self diffusion coefficient vs. pressure isotherms of octamethylcyclotetrasiloxane.

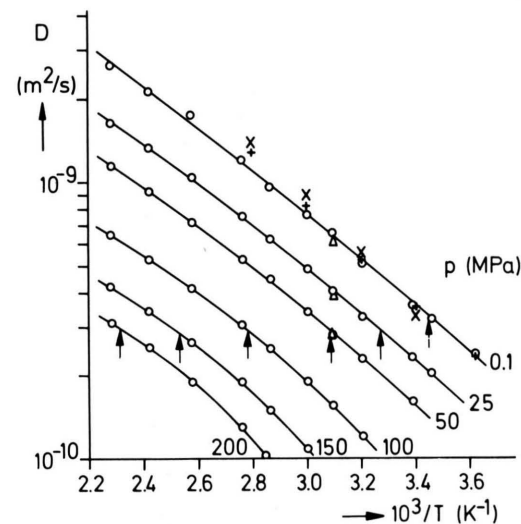


Fig. 5. Arrhenius plot of self diffusion coefficient isobars for octamethylcyclotetrasiloxane. The lines drawn through the experimental points result from a least square fit to the VTF equation. The arrows indicate the melting temperatures at the various pressures. + Data taken from [14], × data taken from [15], △ data taken from [16]. These data were not included in the least squares fitting.

ceases. The solid lines, drawn through the experimental points of Figs. 4 and 5 result from a least squares fit of our self diffusion data to the VTF equation. The data from the other sources for OMCTS quoted above are not included in the fit, since they only cover a very limited range of the T, p space.

The optimal fit parameters obtained are compiled in Table 1. It must, however, be emphasized that the experimental data end far above the ideal glass transition temperature T_0 . For a comprehensive test of the applicability of the VTF equation obviously the data close to T_0 are most critical. The fit parameters given in Table 1 thus carry a significant uncertainty.

For the monohydric alcohols methanol and ethanol [7] the temperature dependence of D could be described by one constant pre-exponential factor D_0 for

CH_3OH , CH_3OD and $\text{C}_2\text{H}_5\text{OH}$ and a constant pressure independent ratio B/T_0 for each compound. This significant reduction of the free parameters was not possible for the unpolar substances studied here. A more comprehensive analysis of the data presented can only be given after p, V, T data for the substances studied here become available.

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